



STUDY OF TRACE METALS IN DUTCH MARINE ENVIRONMENT

by

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Duration of study 3rd June 1983 to 1st June 1984. Under the guidance of Rob Nolting, Department of Marine Pollution, Netherlands Institute for Sea Research, Den Burg, Texel, The Netherlands.

1. SUMMARY

The aim of the present study is to get more information about the analytical technique, sampling and treatment of samples, for the determination of trace elements in the marine environment, followed by the occurrence, distribution and transport of trace metals including major elements in the Dutch Wadden Sea, Lake IJssel, river Rhine, Dutch coastal waters, North Sea, and part of the English coastal waters. Special attention is given to Cu- Cd- Pb- Zn- Ni as well in dissolved as in particulated form. Also Fe and Mn are included because of scavenging properties of their hydrous oxide and the usefulness of Mn as a tracer for sediment transport studies.

In view of the very low trace metal concentration existing in natural waters special attention has been taken to prevent contamination during sampling, storage and analysis. For the determination of dissolved elements complexation followed by solvent extraction is followed.

2. INTRODUCTION

The annual river water discharge to the ocean system is estimated to be about 37 400 km³ (BAUMGARTNER & REICHEL, 1975) which is $2.7 \cdot 10^{-3}\%$ of the total volume of sea water. The river water flow carries approximately $15 \cdot 10^{15}$ g of particulate matter and $4 \cdot 10^{15}$ g of dissolved salts per year (MARTIN & MEYBECK, 1979) into the ocean. This dissolved and particulate material is considered to be 10 times greater than that introduced by glaciers and 100 times greater than atmospheric fall out (GOLDBERG 1972). In order to assess the chemical significance of the flux of material to the ocean system it is necessary to study the trace and major elements of rivers, coastal waters, estuaries and open ocean.

The chemistry of particulate matter in seawater has been subject to numerous studies in recent years (SHOLKOVITZ, 1976; SHOLKOVITZ & PRICE, 1980; FEELEY & MASSOTH, 1981; SKEI & NELSON, 1982).

Objectives of study have been manifold:

- (1) Study the association between pollutants and suspended matter
- (2) Using the chemistry of particulate matter to study water masses
- (3) Study the relationship between bottom sediment and suspended matter
- (4) Study the distribution and pathways of various elements in suspension.

The chemical composition of particulate trace and major elements has been recently summarized by MARTIN & MEYBECK (1979). As a first approximation chemical composition of river suspended matter is very close to surficial rocks. However owing to the importance of chemical weathering and resulting transport of dissolved material, the suspended matter is relatively enriched with Al, Fe, Ti and Lanthanides. It is assumed that in a steady state model additional fluxes are required for some elements, namely Br₂, Cu, Mo, Sb, Zn, Pb, Cd and Ni. It is striking to find that most of these elements are also enriched in aerosols and marine suspended matter. These may correspond either to be a world wide pollution or natural process.

An estuary provides a very varied chemical environment basically defined by a strong salinity gradient (BURTON & LISS, 1976; DUINKER & NOLTING, 1976, 1977, 1978, 1982; MEADE, 1972). It is the meeting place where river water mixes with sea water of a much higher ionic strength. However some transitional elements and nutrients are much more abundant in river water than in sea water. The intensity of different physico chemical and bio-geo-chemical processes can vary with time. Their relative importance in fixing the composition of water will depend on the state of the tide and the magnitude of river flow. These phenomena are compounded by the settling of organic rich particulate matter and subsequent deformation in anionic interstitial waters. Behaviour of many elements appears to vary from one estuary to another, and can often show distinct seasonal, even diurnal, variation in a particular estuary (BEWERS & YEATS, 1980). DUINKER (1980) concludes that evidence for desorption of trace metals from river borne suspended matter upon contact with sea water is very limited. On the other hand conservative behaviour and net removal of river borne dissolved trace metals has been observed for Fe, Al, Cd, Cu, Zn in several estuaries. The removal processes is apparently more important than release that might take place. Trace metals are also subject to internal biogeochemical cycles within the estuary (TUREKIAN, 1977). Physical processes were reported to dominate the total annual budgets of Mn, Fe, and Zn in the Newport river estuary despite the high biological productivity. It can be concluded that only a very limited part by the river transported load of trace metals may reach the ocean. Only those elements that form very strong anionic complexes may be transported out of the estuary in dissolved form (TUREKIAN, 1977).

It is more difficult to assess the situation with regard to the other elements in the dissolved phase. The most common approach is the comparison of the actual distribution of a given element with that predicted from the theoretical dilution curve obtained from the endmembers of river and sea water whereas the salinity is being considered as a conservative index of mixing. Recently much attention was given by many workers to study the dissolved trace metal content in natural waters. (DANIELSSON *et al.*, 1978; BRULAND *et al.*, 1979; DANIELSSON, 1980; BOYLE & HUESTED, 1983; BRULAND & FRANKS, 1983; DANIELSSON & WESTERLUND, 1983).

2.2. DUTCH COASTAL WATERS

The Wadden Sea is a shallow coastal sea much influenced by tidal action, along the western and northern coasts of Denmark, Germany and the Netherlands. Towards the North Sea it is bounded by 17 large inhabited barrier islands as well as numerous small uninhabited sand banks and tiny islands. The boundary towards the mainland is characterized by salt marshes and seawalls. Three large rivers have estuaries opening into the Wadden Sea (Ems, Weser and Elbe).

Approximately 10% of the water and 50% of the suspended matter supplied by the Rhine to the North Sea enter the Dutch Wadden Sea. According to DUINKER (1976) the water in the western part of the Dutch Wadden Sea contains 7% Rhine water and 7% Lake IJssel water. Lake IJssel water is composed mainly out of Rhine water supplied by the river IJssel. The west east transport of water within the Wad-

den Sea is very limited; on the other hand fine grained suspended matter from the North Sea is accumulated within the Wadden Sea toward the eastern part.

The aim of the present study is to get information on the occurrence, distribution and effects of trace elements in the Wadden Sea, river Rhine, Dutch coast, North Sea, English coast and adjacent areas. River Rhine has a marked influence on the quality of the Wadden Sea ecosystem. In this view, dissolved and particulate trace metals have been measured, in order to determine the relative importance of precipitation, sedimentation and flocculation as compared to mobilization and resuspension processes in the estuary and their impact on trace metal levels. Attempts were made to distinguish between the various trace element concentrations in relation to salinity, pH and total seston concentration.

A method for distinguishing between metal fractions that become readily available (adsorbed), organically bound, in oxide coatings and residual fractions, that only may become available after chemical changes (in crystal structure) is used. Chemical leaching procedures are used to extract elements from specific binding sites in suspended matter, although it has got limited quantitative value, because modification from the natural state by aggregation during sampling and separation techniques (filtration, centrifugation) is expected to occur. However they can supply at least qualitatively useful data.

The concentration of suspended matter in the open ocean is low. But this is not valid in shallow and productive areas with considerable larger concentration of particles. Also the total seston concentration in rivers can be quite high. So it is also important to find the relation between the concentration of elements and total suspended matter per unit volume to understand the details of compositions and contribution.

Acknowledgements.—I must express my sincere gratitude to those persons who have cooperated with me during my study at this institute.

First I must mention Mr Rob Nolting who has constantly helped me in my analytical works and during the cruises on board. Thanks also goes to him for his valuable discussions.

Thanks to Dr D. Eisma, Dr T.C.E. van Weering, Miss Yolanda van Iperen, Mr G. Berger, and Mr J. Kalf for their kind cooperation extended to me during my stay in Holland. I am grateful to Mrs Joke Hart for her sincere help.

3. CRUISE PROGRAMME FAROE-ISLAND 9/6-21/7 1983 ON BOARD R.V. TYRO

INTRODUCTION

In connection with the geological study in North Atlantic and North Sea a cruise programme was conducted on board the R.V. Tyro. Purpose of the cruise was to study:

- (1) Exchange of cold arctic water over the Iceland-Faroe ridge
- (2) Sedimentation rate

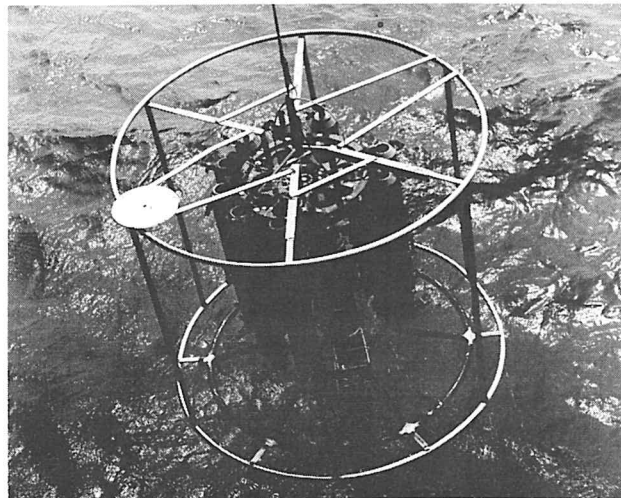
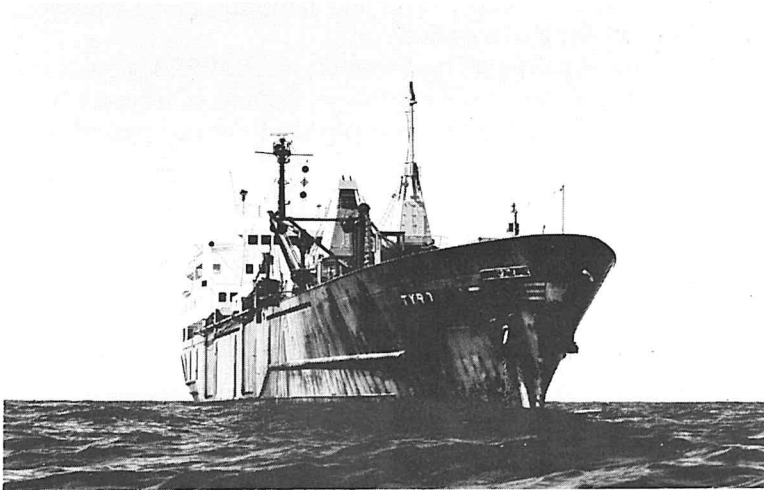
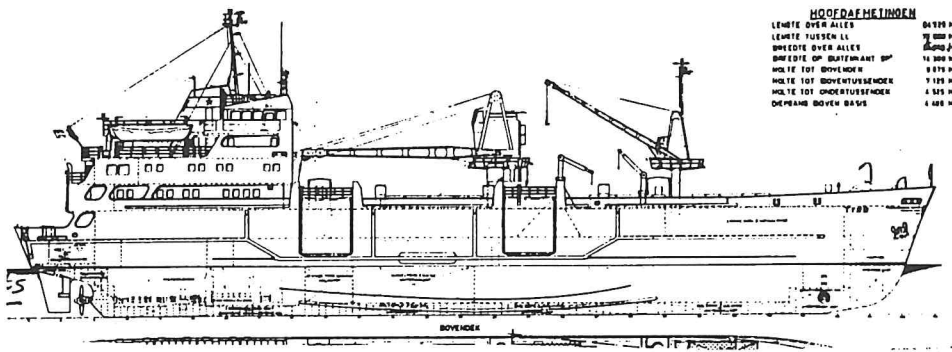


Fig. 1. a. MS Tyro. b. Rosette frame with Niskin sampling bottles and CTD probe.

- (3) Behaviour of the suspended matter
- (4) Sedimentological study of core samples
- (5) General oceanography

3.1. PROGRAM FAROE-ICELAND 9/6-21/7 1983

- 9-6 Departure Den Helder
- 10-6 To German Bight, collection of 7 boxcores, then to Skagerrak
- 12-6 Watersamples transect A, then on to transect B
- 14-6 CTD-stations + watersamples on a number of stations along transects B and C. Boxcore at the end of transect C
- 17-6 Meeting with pilot-vessel from Torshavn (Far-Oe) for disembarcation of J. van Weereld and H. Hobbelink. Then sampling along transects D-O and pistoncore along two stations
- 2-7 Departure Torshavn, sampling along transects S-AB. CTD + watersamples at a number of stations. Boxcores at the end of transect X and on our way to Reykjavik near to the Vestmannaeyjar (volcanic islands)
- 20-7 Arrival Reykjavik

NB. From the results of S, T and turbidity, they will determine on board where water samples will be collected. Bottom sampling stations subject to changes.

3.2. DESCRIPTION OF SHIP AND EQUIPMENT ON BOARD (FIG. 1)

Length: 80 m, breadth: 14.30 m, draft: 4.6 m, tonnage: 1200 (net), max. speed: 14 knots.

The ship has a capacity of 30 containers 7.3 m². The containers were used as laboratories for different disciplines. It has got a satellite navigation and a short wave radio communication system.

The following equipments were carried on board:

- (1) Piston corers
- (2) Box corers
- (3) Coulter counter model TA II (Fig. 3)
- (4) Echosounder
- (5) Salinometer (Beckman Intsr. Inc.) (Fig. 3)
- (6) CTD and computerized printer recorder
- (7) Niskin Bottles (G-O) and Rosette sampler
- (8) Millepore vacuum filtration unit
- (9) Shipboard stirred pressure filtration system with purified nitrogen atmosphere
- (10) Sample Bottles (glass)
- (11) Prewieghed Sartorius membrane filters (0.45 um pore size) in Petri dishes

New stainless steel hydrowire terminated with a nylon coated Pb weight was used for all oceanographic winches.

3.3. METHODS AND SAMPLING

Core samples were collected by piston corers. Plastic core boxes, containing samples from piston corers were cut in two sizes, top and bottom. Immediately covered with plastic caps on both the ends and covered in plastic papers. The samples were kept in the deep freeze. Samples from box corers were kept in the core box, covered with plastic papers and preserved in the deep freeze as well.

Water samples were obtained by using modified Niskin bottles (12 ltr) mounted in a Rosette frame, together with a Guildline CTD (Conductivity, Temperature, Depth) probe, and a turbidity meter. Closing the Niskin bottles at a particular depth was triggered off by an electrical sensor. Turbidity, salinity, temperature, depth of the vertical profile were continuously monitored by a computerized strip chart recorder (Hewlett Packard) attached with the CTD instrument. Occasionally the salinity readings from the probe were checked by salinometer with samples obtained from the sampler. Calibration was made with IAPSO standard sea water. The temperature reading of the probe was calibrated using reversing thermometers. The turbidity was measured with a Zaneveld transmissometer coupled to the CTD.

Turbidity expressed in Volts (V) is a relative measurement. It has got a relation with total suspended matter concentration ($\text{mg}\cdot\text{l}^{-1}$). The level of chlorophyll a in the near surface water gives an indication of the productivity at the time of sampling. Plankton cell counts, particularly those of diatoms can be related to a supply of nutrients transported by fresh water.

The total concentration of suspended matter was determined by filtering the sample over a preweighed $0.4\ \mu$ membrane filter. The membrane filter was fitted in a plastic holder attached to a filtration system using N_2 gas for pressure. The suspended matter was washed with distilled water in the same holder under N_2 gas pressure. Ash weight was determined after heating the sample to a 550°C for 8 hours by weighing on a Cahn Microbalance. Particle size was determined directly on board with a Coulter Counter Model TA II. The Coulter counter gives number of particles and particle size. It is expressed as number of particles per size fraction, in volume percentages.

For chlorophyll analysis, one litre of sample was filtered through GF/C glass fibre Whatman filter paper on which a layer of hydrated MgCO_3 was precipitated (by pouring a few ml of 1% MgCO_3 solution). Filter papers containing chlorophyll on magnesium carbonate were immediately deep frozen. It was measured fluorometrically according to the methods of YENTSCH & MENZEL (1963) and STRICKLAND & PARSONS (1972). Aliquot samples were kept in 50 ml bottles with JKJ as a preservative for plankton that was counted in the lab with an inverted Zeiss Microscope.

For studies of the suspended particulate matter with a Scanning electron Microscope; 20 ml of water samples were vacuum filtered over nucleopore membrane filters. It was washed three times with absolute alcohol and kept in petridishes till analysis.

For major element analysis of the particulate matter, 0.5-4 litre from the water samples was pressure filtered with N_2 gas through a $0.45\ \mu$ nucleopore membrane

filter that was kept in a filter holder. While still wet the membrane was rinsed with 50-100 ml of distilled water. The suspended matter is to be analysed for major elements by X-ray fluorescence (D. Eisma).

4. SAMPLING ON BOARD R.V. NAVICULA 30/1-2/2 1984

4.1. INTRODUCTION

As part of a research programme a cruise in the Wadden Sea was organized by NIOZ with the research vessel MS "Navicula". Water samples were taken at different stations as indicated in Fig 4. Extreme precautions were taken to avoid contamination during all steps of sampling and further steps. Mainly surface samples were taken.

4.2. DESCRIPTION OF VESSEL (SEE FIG. 2)

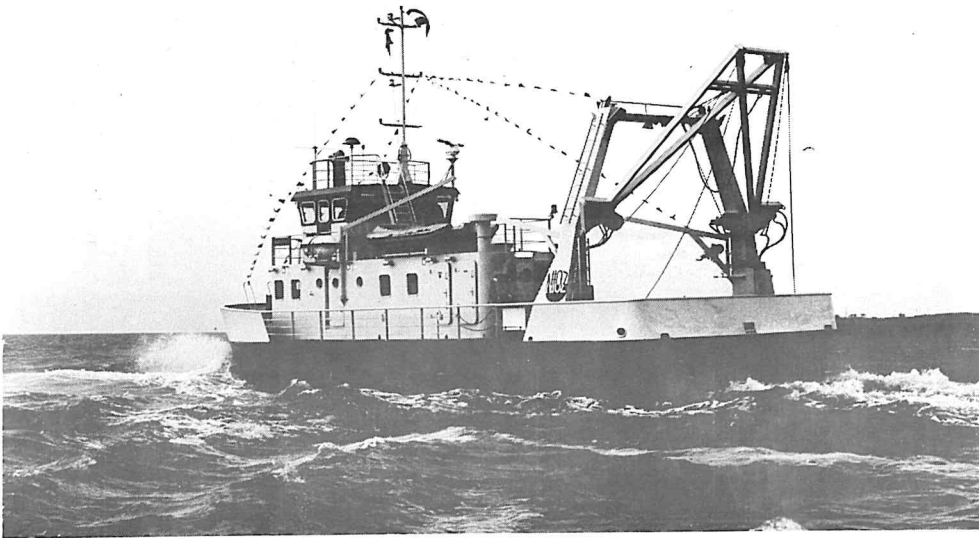
The vessel was built and equipped for work particularly in the shallow waters of the Wadden Sea. Specifications are as follows: length: 21.25 m, breadth: 7.00 m, draft: 1.00 m, max. speed: 7 knots, tonnage: 40 000 kg (net), endurance: 10 days.

The vessel has two DAF diesel engines of 135 HP each and an attached Zephyr rubber boat. She is fitted with Furrino radar FR-1011-n and a gyro compass for navigational purpose. During the cruise, position fixation was done with the help of buoys which mark the channels in the Wadden Sea at various points. The vessel has an echosounder (Lowrance 2460MA, USA) and radio telephone type RT 4413. A removable multipurpose type container was fitted on board for laboratory works. It was fitted with an A-frame, for fishing and core sampling purposes, and two winches of 2.5 ton breaking strength having 70 m long wire of 12 mm diameter for hydrographic work.

4.3. SAMPLING SCHEME AND METHODS

Surface samples were collected from Wadden Sea and Lake IJssel. They were collected from the rubber boat which was about 500 m away from the ship. Water samples were taken in one litre high density polyethylene bottles, while the hands were covered with plastic gloves. After sampling the bottles were put in plastic bags for protecting against contamination. Back on the Navicula water samples were immediately filtered in an all teflon nitrogen pressurized filtering unit (made in NIOZ; Fig. 5) on preweighed 0.45μ pore size nucleopore membrane filters, to separate the suspended matter from the water phase. Along with the water samples for trace metal determination also water was sampled in a polypropylene bucket that was required for determination of pH, salinity and temperature. pH was determined with a Knick pH meter, which was daily calibrated with buffer solutions; salinity and temperature were determined with a switchgear apparatus (Fig. 6). After filtration of the water samples (1 litre) in the same bottles they were acidified by adding a 0.5 ml suprapure HCl. Additions were made by means of a

a



b

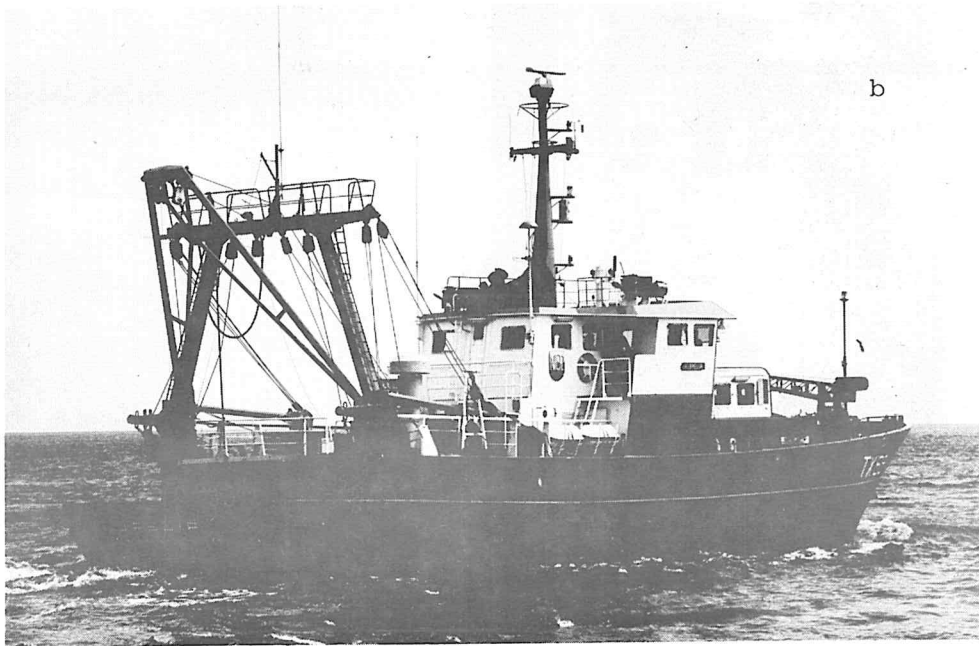
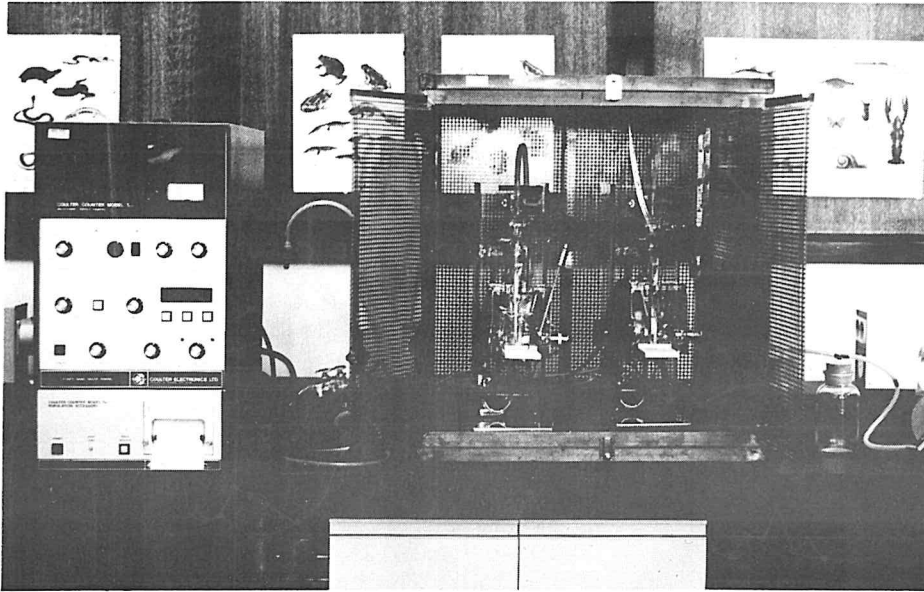
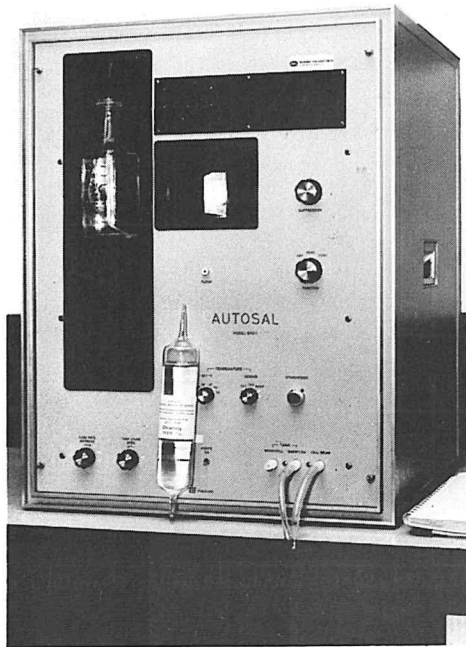


Fig. 2. a. MS Navicula. b. MS Aurelia.



a



b

Fig. 3. a. Coulter Counter TAIL. b. Salinometer (Beckman Instr. Inc.).

micropipette supplied with disposable tips. The suspended particulate fraction on the membrane filter was washed three times with double distilled water and kept in covered petri dishes.

It may be mentioned here that all the one litre sampling bottles and nucleopore membrane filters were extensively cleaned prior to the cruise. Bottles were shaken two days on a shaker filled with 6N HCl, then washed several times with deionized water and next with double distilled water. The membrane filters were kept in 6N HCl for a few days, then washed several times with double distilled water to free it completely from the acid, dried at 60°C then weighed and kept in petridishes. The

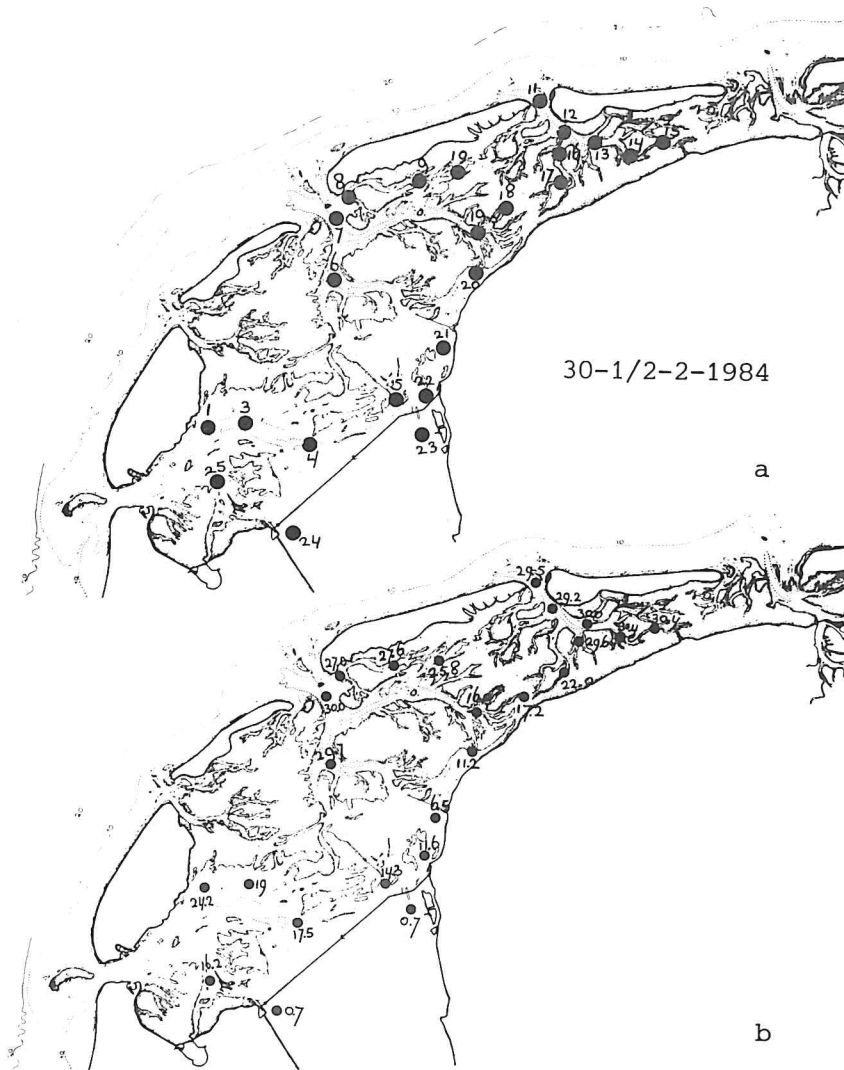


Fig. 4. a. Sampling stations during trip W43 and b. Salinity ($S \cdot 10^3$).

teflon filtering unit was first washed with 6N HCl and then with double distilled water.

The acidified water samples and suspended particulate matter were taken to the laboratory for analytical works.

5. SAMPLING ON BOARD AURELIA 27/2-1/3 1984

5.1. INTRODUCTION

To take samples in the North Sea and from River Rhine another cruise was organized by NIOZ on board the research vessel "Aurelia". Surface samples were taken from a rubber boat in the same way as in the Wadden Sea, and also by Go-Flo samplers. The estuary of the Rhine and North Sea within and through the salinity maximum were included in the scheme. Few samples were also taken near the English coast. In Fig. 7, the cruise track is shown where also the salinity of the sampling stations are given.

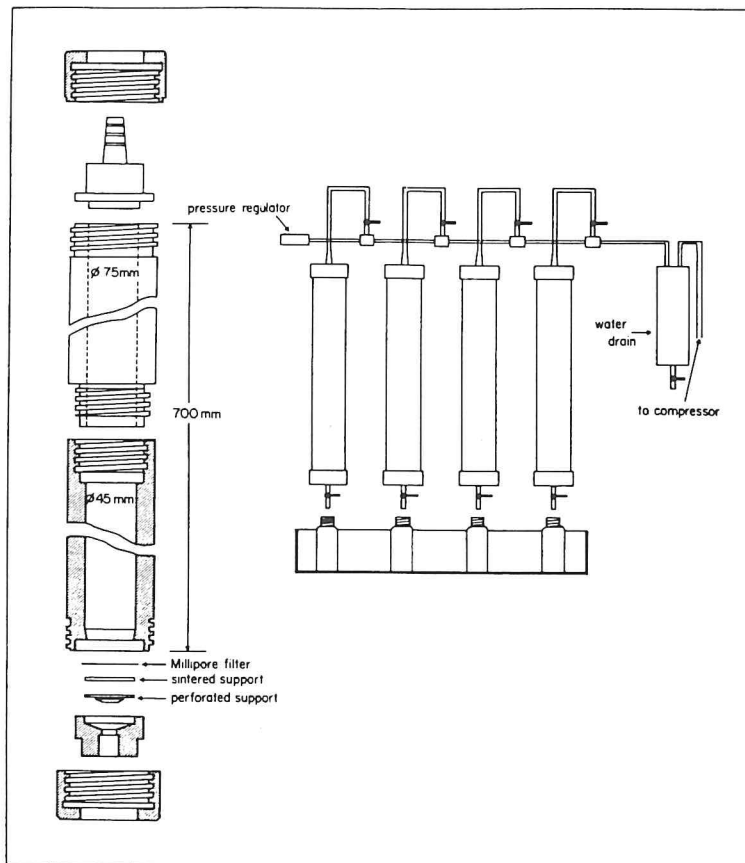


Fig. 5. Filtration system with details of one of the all-Teflon units.

5.2. DESCRIPTION OF VESSEL (FIG. 2)

This vessel was built and equipped to work as well in coastal areas as in open sea. Specification are as follows: length: 31.75 m, breadth: 7.50 m, draft: 3.50 m, max. speed: 10 knots, tonnage: 100 ton (net), endurance: 15 days.

Regarding navigational and communication equipment it was equipped with Decca-Navigator MK21, Decca-Askas Sea track, Decca-Pilot 650, Decca-radar RM914. An echosounder-Atlas Echograph 470. Radio Holland communication SAILOR type T-122. The following winches including hydrographic winches were available.

A 300 kg winch with a 300 m long hydrographic 6 mm wire, a 5 ton winch with a 300 m long oceanographic 15 mm wire, working with an A-frame. A Zephyr rubber boat with a Mercury petrol engine was also supplied. Two fixed labs (7 × 3 m) were on board for laboratory work equipped with a drying oven and a deep freeze.

5.3. SAMPLING SCHEME AND METHODS

Sampling was done in the same manner as described earlier during the cruise of "Navicula". Only during the sampling on river Rhine, water samples were taken



Fig. 6. Salinity temperature bridge (Electronic Switchgear MC5).

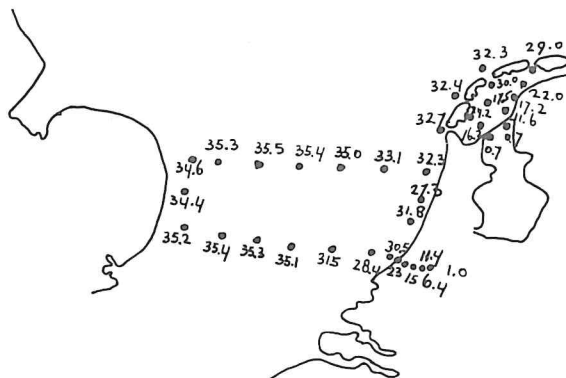


Fig. 7. Sampling stations with salinity ($S \cdot 10^3$) during North Sea trip N16, also including data obtained during trip W43.

by a Go-Flo-water sampling device Model 1080 (Fig. 8). It was lowered by means of a hydrographic winch and a messenger was sent to close the sampler. pH, salinity and temperature were measured from water samples taken in a polypropylene bucket. The filtering procedure was the same as already described by the Navicula trip. In the middle of the North Sea duplicate samples were taken, one was filtered, the other not. A 0.5 ml suprapure HCl was added as well to the filtered as to the unfiltered samples. All the samples were taken to the laboratory for further studies and analytical works.

6. ANALYTICAL WORKS

6.1. DETERMINATION OF SUSPENDED PARTICULATE METALS

6.1.1. REAGENTS AND EQUIPMENT

(1) A Perkin Elmer type 403 Atomic Absorption Spectrofotometer fitted with a Hitachi strip chart recorder Model 056-1002 and background corrector (Deuterium Arc power supply). This instrument is used for measurements with air-acetylene and nitrous oxide acetylene flames only.

(2) A Perkin Elmer 5000 AAS. Fitted with a Perkin Elmer HGA-500 graphite furnace and a AS40 ato-sampler. Absorbance peaks were recorded by means of a Perkin Elmer 56 strip chart recorder (Fig. 9).

(3) Graphite tubes, some with pyrolytically coating

(4) Micropipette, microtips

(5) Teflon bombs

(6) Low temperature Asher Tracer Lab 505

(7) Suprapure HNO_3 , HCl, HF and Boric acid

(8) Polypropylene volumetric flasks

- (9) Millipore filtration unit
 (10) Standard solutions of the elements of interest were prepared from Titrisol (Merck)
 (11) Hollow cathode lamps for Fe, Al, Si, Ca, Mg, Na, K, Zn, Mn, Cr, Ni, Cu. Electrodeless discharge lamps for Cd and Pb.

6.1.2. PROCEDURES

All sample preparations were done in a clean laboratory equipped with laminar flow benches. The suspended matter on the membrane filters were dried in an oven for 2 hours at 60°C and weighed after cooling. This and the difference of the previous filter weight gives the suspended matter concentrations of the samples. Now the sample is ready for decomposition.

To determine the leachable fraction of the suspended matter, the membrane filter with suspended matter was first put in a low temperature asher, where a stream of low pressure oxygen excited by radiofrequency discharge is used to

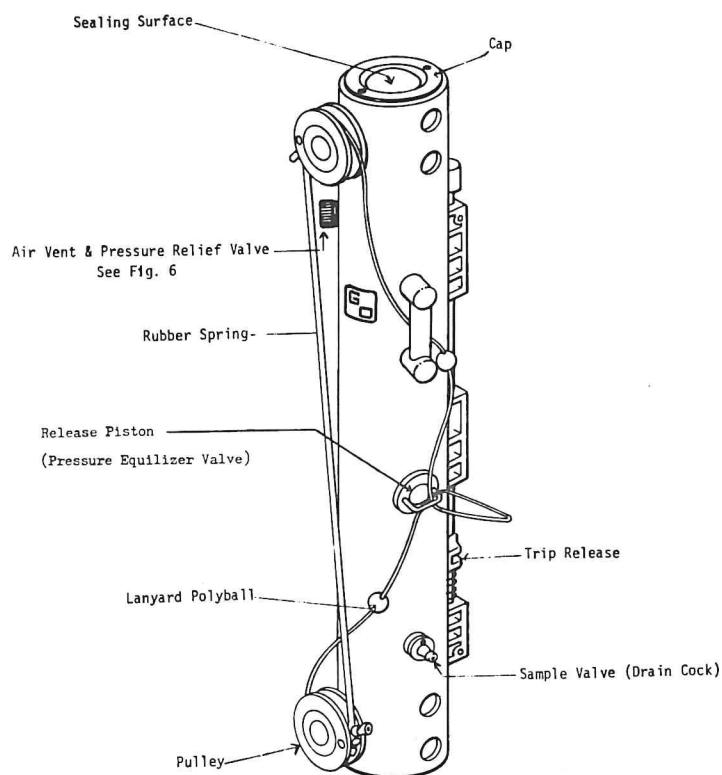


Fig. 8. Go-Flo sampling bottle (General Oceanics model 1080).

decompose the filter, which is inserted in a closed borosilicate glass reaction chamber. A variable power of 0-400 watts is supplied by a conventional radiofrequency oscillator.

Ashing condition: power: 200 watt, pressure: 1mm Hg, O₂ flow: 40 ml·min⁻¹, time: 1.5 hours.

After ashing the remaining particulate matter is transferred to a 50 ml polyethylene volumetric flask with a 0.1 N HCl solution and made up to the mark. After shaking thoroughly this is kept overnight. Next day it was filtered through a membrane filter (0.45 μm pore size) using a Millipore filtration unit, while vacuum was obtained with a suction motor. So leachable and residual fraction are separated. The residual fraction on the membrane filter is placed on the bottom of a teflon bomb with plastic tweezers. One ml of aqua regia (3:1 mixture of suprapure HCL: HNO₃) and 5 ml of suprapure HF are added and the cover placed on tightly. The bomb is kept in a drying oven at 110°C for 2 hours. After cooling the content of the vessel is poured through a polypropylene funnel into a 50 ml polyethylene vol. flask containing 30 ml of saturated boric acid solution. The teflon bomb is washed with little double distilled water which is added to the flask, this is made upto the volume and shaken. Also a blank solution is prepared. So we have a leachable and a residual fraction that are ready for measurement. For calibration normally standard addition methods are applied.

By flame AAS the following elements were measured:

- using nitrous oxide/acetylene: Al, Si, Ca, Mg, Ti
- using air/acetylene: Fe, Mn, Zn, Na, K

By flameless AAS the following elements were measured:

- Cd, Pb, Ni, Cu, Cr, Co and also sometimes Fe and Zn.

6.2. DETERMINATION OF DISSOLVED METALS

6.2.1. REAGENTS AND EQUIPMENT

(1) Ammonium Pyrrolidine Dithiocarbamate (APDC) and Diethyl ammonium diethyl dithiocarbamate (DDDC). The extractant solution was made by dissolving 1.0 g of APDC and 1 g DDDC in 100 ml water. This solution was purified by extracting three times with MIBK, and kept at 4°C. It can be used for 2-3 days.

(2) Buffer solution: (2M ammonium acetate) was made by mixing 118 ml of 96% acetic acid and 225 ml of 25% ammonia liquor into 500 ml water and diluting to 1 litre. Buffer is checked before use.

(3) MIBK

(4) Nitric Acid. Hydrochloric Acid. Ammonia. Acetic Acid. All are of suprapure quality.

(5) Stock standards were made from Titrisol standards (Merck)

(6) Teflon separatory funnel of 1000 ml volume

(7) Micropipettes

Ultra clean water was obtained from a Milli Q purification system. The Perkin Elmer 5000 AAS with HGA 500 graphite furnace and AS-40 Autosampler is used

for sample measurement. Teflon sample containers of 25 ml were used for storing the extracted solution. All the teflon labware was cleaned as follows: They were filled with 6N HCl (ultrapure) for one week. Then the acid was discarded, and they were several times carefully rinsed, with double distilled water.

6.2.2. PROCEDURES

All works were carried out in a clean laboratory container equipped with clean air laminar flow benches. To 500 ml of sea water (molarity of solution 1 ml HCl in 1 litre) 3 ml of buffer solution was added to obtain pH 4 to 4.5 which was checked with a pH meter. Now 2ml APDC/DDC mixture was added and mixed with the sample. After this 20 ml of MIBK was added and the mixture was shaken for 2 minutes. After phase separation (waiting 2 min) the sea water was discarded. The organic phase was rinsed with 10 ml bidest. water to remove remaining salt, and after separation the water was discarded. Now 0.5 ml of conc. HNO_3 (suprapure) was added and a reaction time of 20 min was allowed. Then 9.5 ml double distilled water was added and the solution shaken for 0.5 minutes for back extraction. After phase separation the aqueous phase was collected in the precleaned teflon containers. Sample blanks were made by extracting 10 ml and 500 ml by the Mill-Q system purified water. 1 ml of suprapure HCl was added and it was extracted by the same procedure as the samples (DANIELSSON *et al.*, 1978).

Standard Blank: The extracted seawater was saved from a set of samples in a clean bottle (about 3 litre). The seawater was extracted with an additional amount of MIBK to remove any residual trace elements. The cleaned seawater was partitioned amongst six separatory funnels. One as a blank and others were spiked with various mixed standards. 2 ml APDC/DDDC solution and 20 ml MIBK was added and the same procedure was applied as previously. Standards were thus

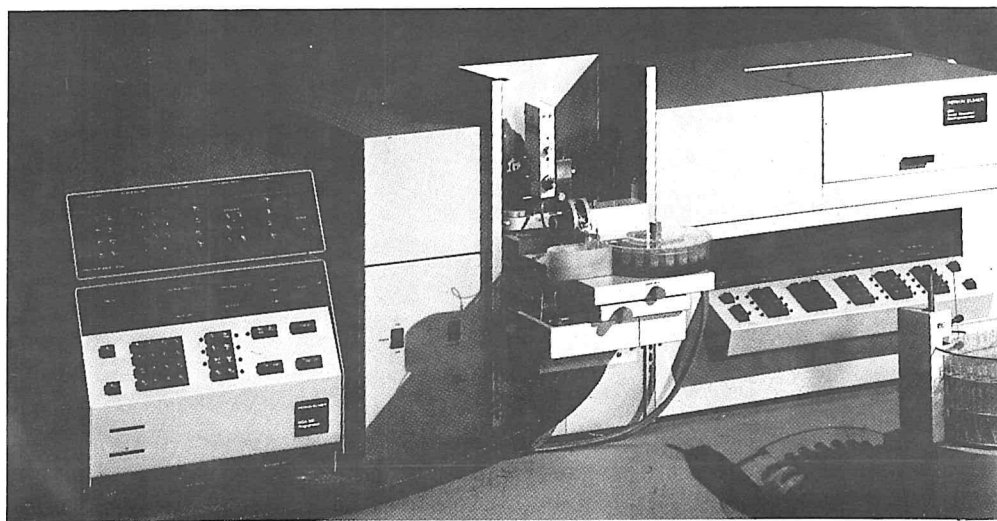


Fig. 9. Perkin-Elmer model 5000 A.A.S., fitted with a H.G.A. 500 graphite furnace and a A.S. 40 atomizer.

prepared of the following concentrations:

1, 2, 4, 5, 10 $\mu\text{g}\cdot\text{l}^{-1}$ for Fe, Cu, Ni, Zn and

0.1, 0.2, 0.4, 0.5 1.0 $\mu\text{g}\cdot\text{l}^{-1}$ for Cd and Pb

After extraction the metals were determined by graphite furnace A.A.S. The operating conditions are presented in Table 1. It is however necessary to mention that the temperature programmes for the element differ considerably depending on the sample. For Cd and Pb about 2 hours warming up of the lamp is required. Peak heights were used for evaluation in all cases.

TABLE 1

Example of graphite furnace heating conditions for trace metal determination in HNO_3 after back extraction from MIBK: (a) ramptime in sec.; (b) holdtime in sec.; (c) temperature in $^\circ\text{C}$; (d) ml $\text{N}_2\cdot\text{min}^{-1}$.

<i>Metal</i> (μl)	<i>Sample volume</i>	<i>Drying step</i>	<i>Charring step</i>	<i>Atomization step</i>	<i>Cleaning step</i>	
Cd	20	1	1	1	1	(a)
		20	20	6	1	(b)
		100	250	2100	2500	(c)
		300	300	50	300	(d)
		Exp. 0.5			Normal tube	
Pb	20	10	10	1	1	(a)
		40	20	4	2	(b)
		110	880	2300	2700	(c)
		300	150	0		(d)
		Maximum power heating			Normal tube	
Cu	20	10	10	0	1	(a)
		20	20	5	1	(b)
		130	900	2200	2500	(c)
		300	300	50	300	(d)
		Maximum power heating			Normal tube	
Ni	20	10	10	0	1	(a)
		30	20	6	1	(b)
		110	1200	2700	2500	(c)
		300	300	0	300	(d)
		Maximum power heating			Pyrocoated tube	
Fe	20	10	10	0	1	(a)
		30	20	7	1	(b)
		110	1200	2500	2500	(c)
		300	300	0	300	(d)
		Maximum power heating			Normal tube	
Zn	20	10	10	1	1	(a)
		30	20	6	3	(b)
		110	500	2100	2700	(c)
		300	150	50	30	(d)
					Normal tube	

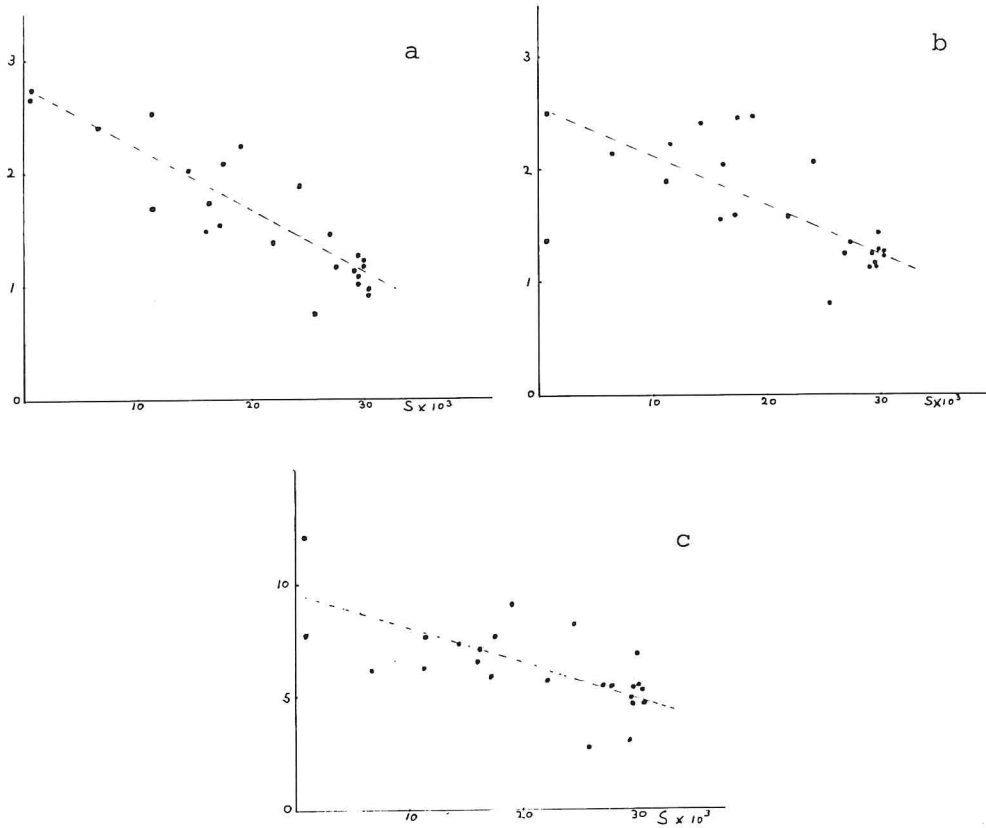


Fig. 10. Dissolved concentrations of Cu (a), Ni (b) and Zn (c) in relation to salinity ($S \cdot 10^3$) during trip W43 (in $\mu\text{g} \cdot \text{l}^{-1}$).

7. RESULTS AND DISCUSSION

7.1. WADDEN SEA

Concentrations of dissolved trace metal are presented against salinity distribution (Figs 10 and 11). A linear relationship has been found for Zn, Cu, Ni and Fe. Fresh water coming out of Lake IJssel is mixed with saline water from the North Sea. The flow of water can be observed from the salinity contour representation. The concentration of Cu, Ni, Fe and Zn are quite high in the mixing area in the western part of the Wadden Sea, for Cd and Pb the concentration does not vary with salinity. From Figs 12, 13 and 14 it is observed that Ni and Cu values in Lake IJssel are not much higher than in the western Wadden Sea, but the values decreasing remarkably in the middle of the Wadden sea, whereas Fe and Zn values are much higher in Lake IJssel and a slight decrease to the middle of the Wadden Sea. Pb and

Cd values in Lake IJssel are higher than the values in the eastern part of the Wadden Sea, but lower than the values in the western part. Fig. 15 gives the comparison of leachable and total concentration of Fe, Ca, Mn, Zn, Mg and K. Fig. 16 gives also the salinity and suspended matter concentration against the stations. It is

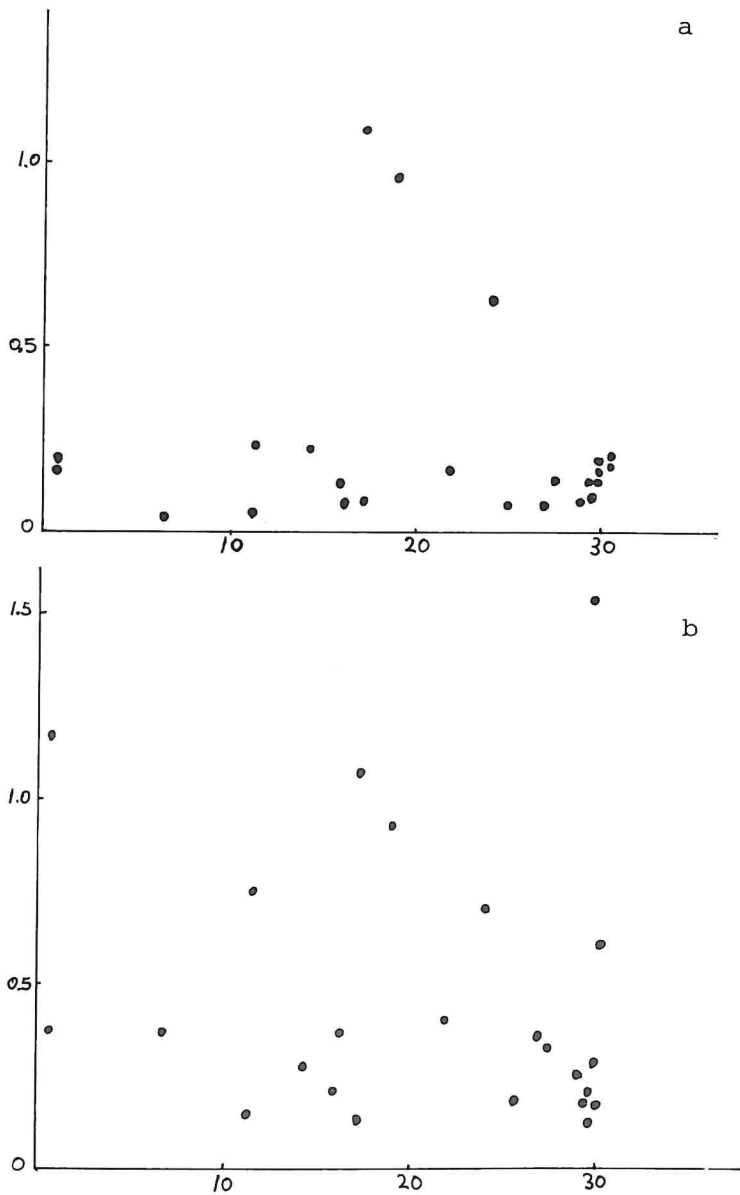


Fig. 11. Dissolved concentration of Cd (a) and Pb (b) in relation to salinity ($S \cdot 10^3$) during trip W43 (in $\mu\text{g} \cdot \text{l}^{-1}$).



Fig. 12. Concentrations of dissolved Cu and Pb (in $\text{nmol}\cdot\text{l}^{-1}$) during trip W43.

observed that K, Mg, Si and Al concentrations are quite low in Lake IJssel compared to the Wadden Sea values. The percent leachable fractions for Zn (65%), Mn (85-90%) and Ca (98%) throughout, whereas Mg and K leachable fraction are very low. For Al and Si it is almost negligible. Mn and Zn concentrations are very high at low suspended matter content, gradually falls with increasing suspended matter content (Fig. 17). In Lake IJssel Al, Si, Mg, Ca content are very low whereas Mn and Zn are very high.

7.2. CONCLUSION

From the above observation it can be concluded that some kind of exchange occurs between the existing interstitial waters and sediment with the overlying water by low tide. So overlying water is enriched with trace elements. Strong wind and tidal action are responsible for the distribution of trace elements. Out of the mixing curve it can also be said that Lake IJssel supplies high concentrations of dissolved Cu, Zn, Cd and Ni to the Wadden Sea. High admixture of fluvial sediment which



Fig. 13. Concentrations of dissolved Ni and Cd (in $\text{nmol}\cdot\text{l}^{-1}$) during trip W43.



Fig. 14. Concentrations of dissolved Zn and Fe (in $\text{nmol}\cdot\text{l}^{-1}$) during trip W43.

is dumped by North Sea in the Wadden Sea, and marine particulate matter are responsible for the enrichment of those metals in the Wadden Sea. For the Pb distribution it is evident that atmospheric fall out, like aerosol formation in the surface layer, is an important factor.

The high river Rhine run off and the constantly blowing eastern wind at the period of sampling makes it possible that we could find for some elements a clear mixing curve, covering the whole salinity regime, while in a normal period only the end member salinities are found.

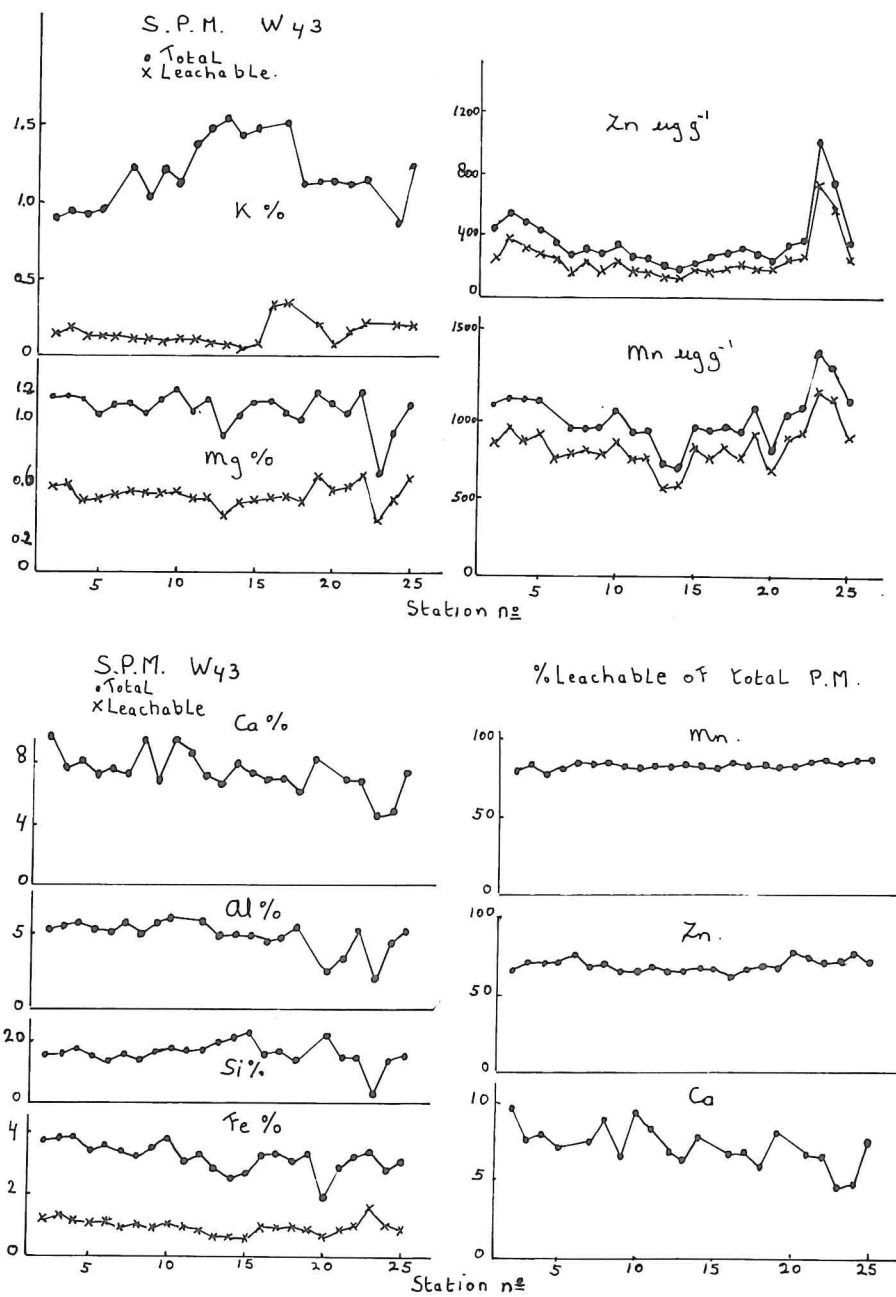


Fig. 15. Total and leachable concentrations of K, Mg, Zn, Mn, Ca, Al, Si and Fe (in % and $\mu\text{g}\cdot\text{g}^{-1}$) in suspended matter, in relation to station number during trip W43.



Fig. 16. Salinity ($S \cdot 10^3$) and suspended particulate matter ($\text{mg}\cdot\text{l}^{-1}$) in relation to station number during W43.

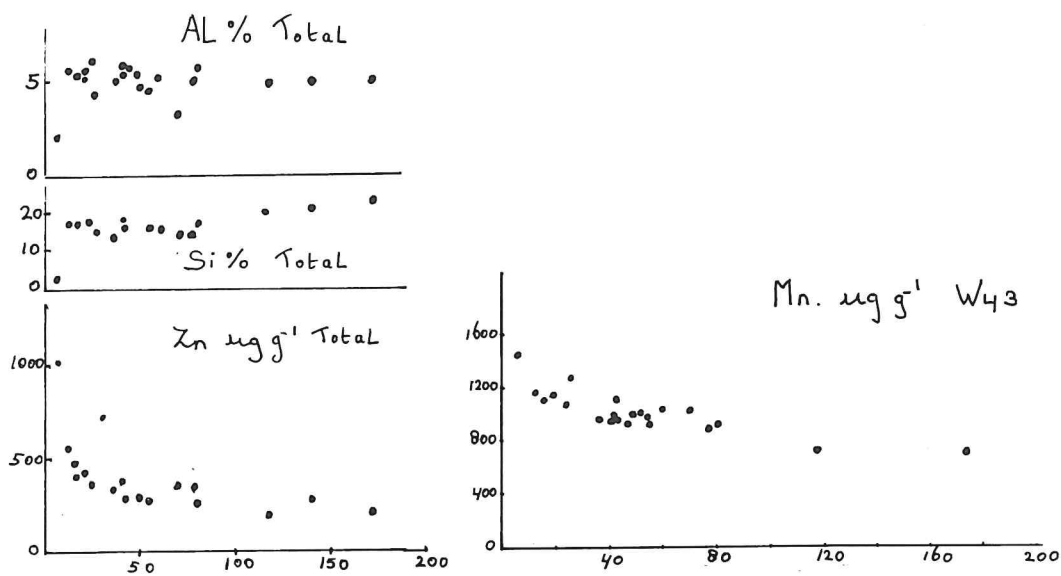


Fig. 17. Total concentrations of Al, Si, Zn and Mn (% and $\mu\text{g}\cdot\text{g}^{-1}$) in suspended particulate matter in relation to suspended matter ($\text{mg}\cdot\text{l}^{-1}$).

7.3. NORTH SEA

Fig. 18 shows near linear relation with salinity for dissolved Cu, Zn, Ni and Cd, for Pb it is confusing. Near the English coast the concentration of Cu, Pb and Zn are quite higher than near the Dutch coast, in spite of the same salinity. Cu, Ni and Fe concentrations, are lower in the northern part and higher in the southern part. Zn and Cd show relatively higher concentration in the northern part than in the southern part. Pb values are higher near the English coast indicating greater flux of aerosol Pb to the region, whereas near the Dutch coast it is mostly dictated by the River Rhine and the Wadden Sea.

Fig. 19 shows concentration of particulate fractions plotted against station. Cu and Cd show similar concentration near the English and Dutch coast where as Mn and Zn show lower values near the English coast. Neither Al, Si or Fe shows any enhancement of value near the coast outside the Wadden Sea. Contents of Mn, Zn, Cd and Cu are quite high in the River Rhine. Ni is a little bit low comparatively because Ni is quite a newcomer as a pollutant. For Fe, Ca and Al slight increased values with the increased salinity is observed. Cu, Mn and Zn are high in river particulates. Cu, Zn, Cd and Ni maintain almost linear relation with salinity which is expected. Fig. 20 represents dissolved concentrations of Pb, Zn, Cu, Fe, Ni and Cd against station numbers. Fig. 21 shows the relation of Zn, Cd and Cu to suspended matter concentrations ($\text{mg}\cdot\text{l}^{-1}$). Fig. 22 shows concentration of Cd, Cu, Ni, Zn, Pb and Fe (in $\text{nmol}\cdot\text{l}^{-1}$) plotted against station number during trip N16, also including some data obtained during trip W43.

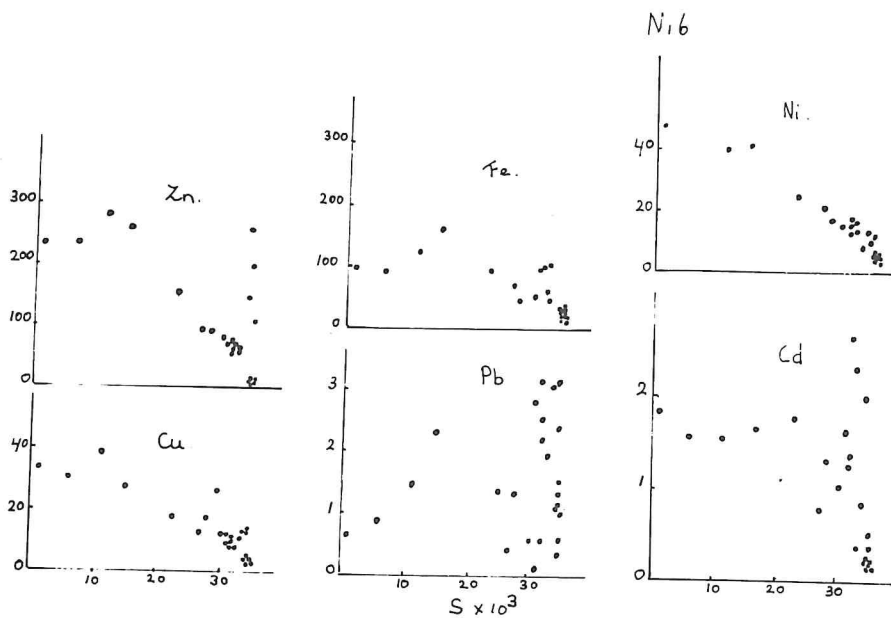


Fig. 18. Concentrations of dissolved Zn, Cu, Fe, Pb, Ni and Cd ($\text{nmol}\cdot\text{l}^{-1}$) in relation to salinity ($S\cdot 10^3$).

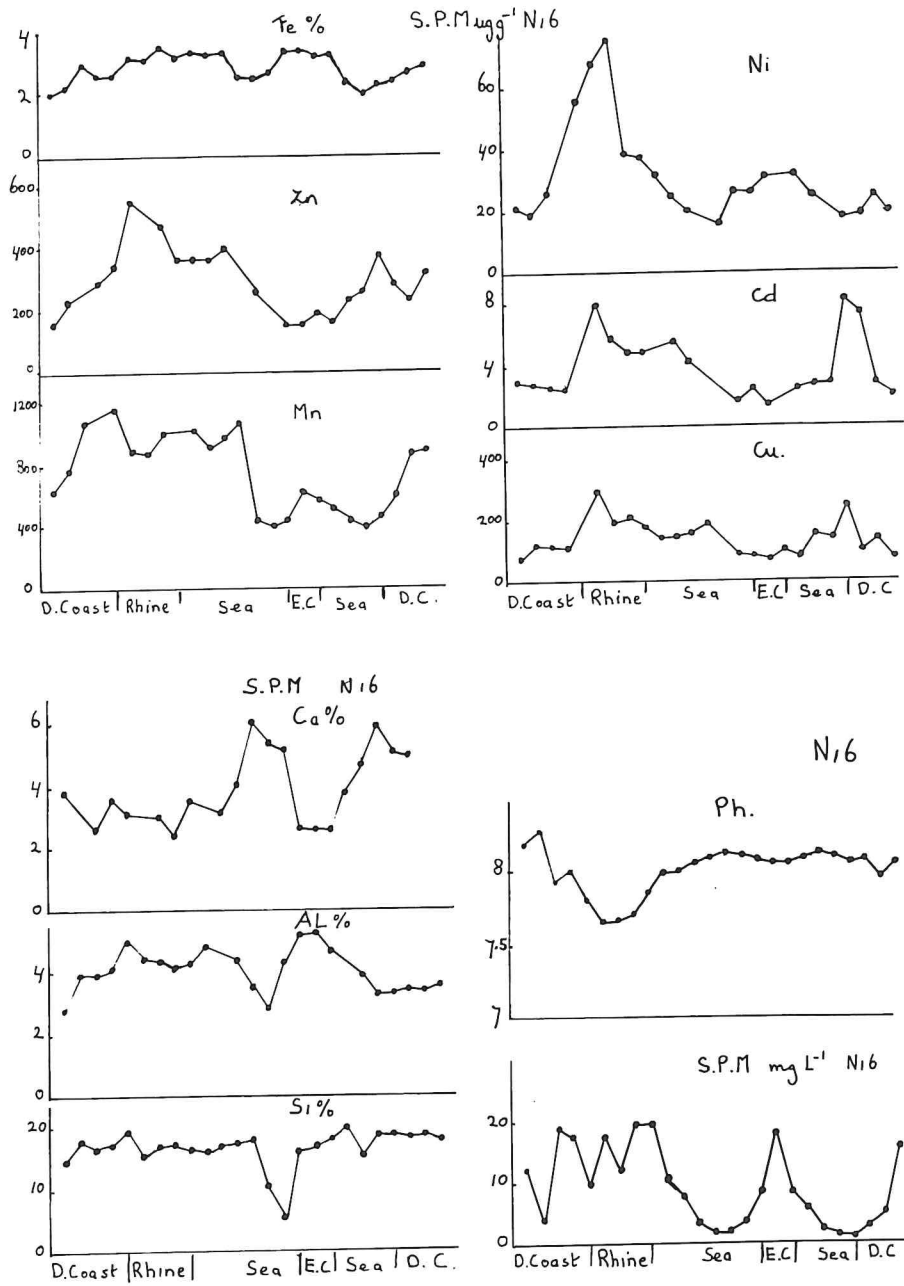


Fig. 19. Concentrations of Fe, Zn, Mn, Ni, Cd, Cu, Ca, Al and Si (% and $\mu\text{g}\cdot\text{g}^{-1}$) in suspended particulate matter in relation to station number (given as specific areas, Dutch coast, Rhine, middle of North Sea and English coast) during trip N16. Also pH and suspended particulate matter ($\text{mg}\cdot\text{L}^{-1}$) is given.

7.4. CONCLUSIONS

From all those observations it can be concluded that trace metal concentrations near the Dutch coast are mostly influenced by the river Rhine and partly by the Wadden Sea. This influence is limited within a few kilometers of the Dutch coast. The higher trace metal concentration near the English coast are due to effects of fluvial particles and land derived terrigenous material. So contaminants in the North Sea are mostly derived from rivers, atmospheric fall out and direct discharge offshore. Zn, Cu, Pb in particulate form are predominantly accumulated in the area where suspended matter is deposited. A strong enrichment of Pb is mainly caused by dumping waste material and aerosol formation. At this time of observations, we did not sample real fresh river water, which turns out in mixing curves of dissolved trace metals in the Rhine estuary, not showing any removal processes as had been observed earlier, but a conservative mixing.

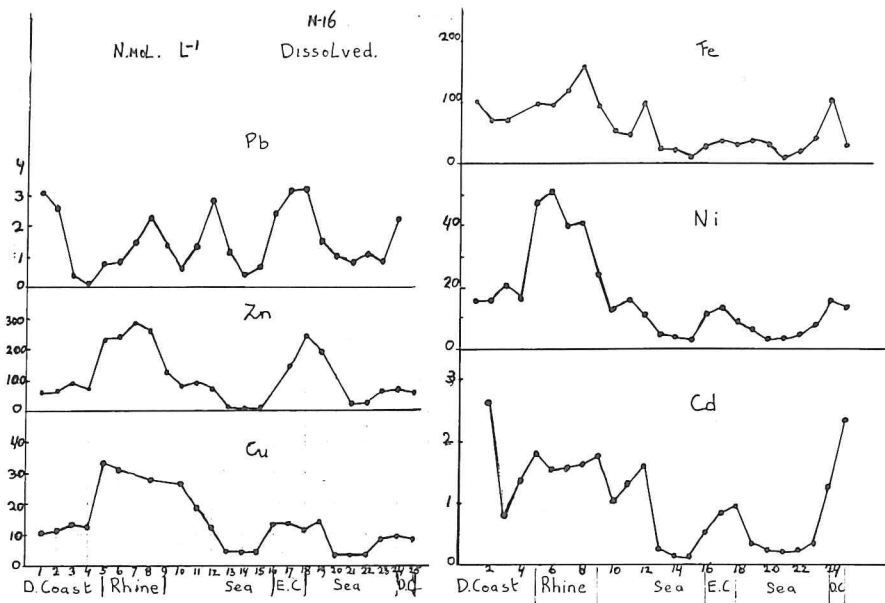


Fig. 20. Concentrations of dissolved Pb, Zn, Cu, Fe, Ni and Cd (in $\text{nmol}\cdot\text{l}^{-1}$) in relation to station number during trip N16.

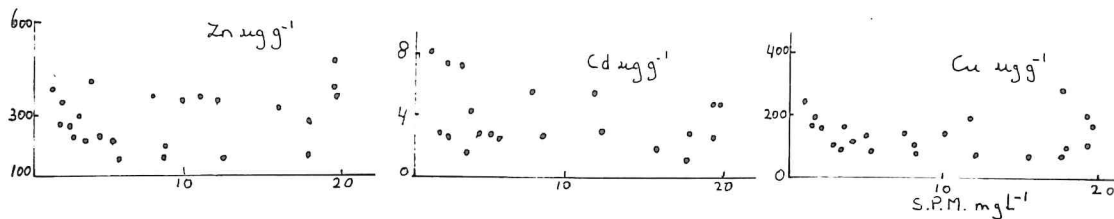


Fig. 21. Concentrations of particulated Zn, Cd and Cu in relation to suspended matter concentration.

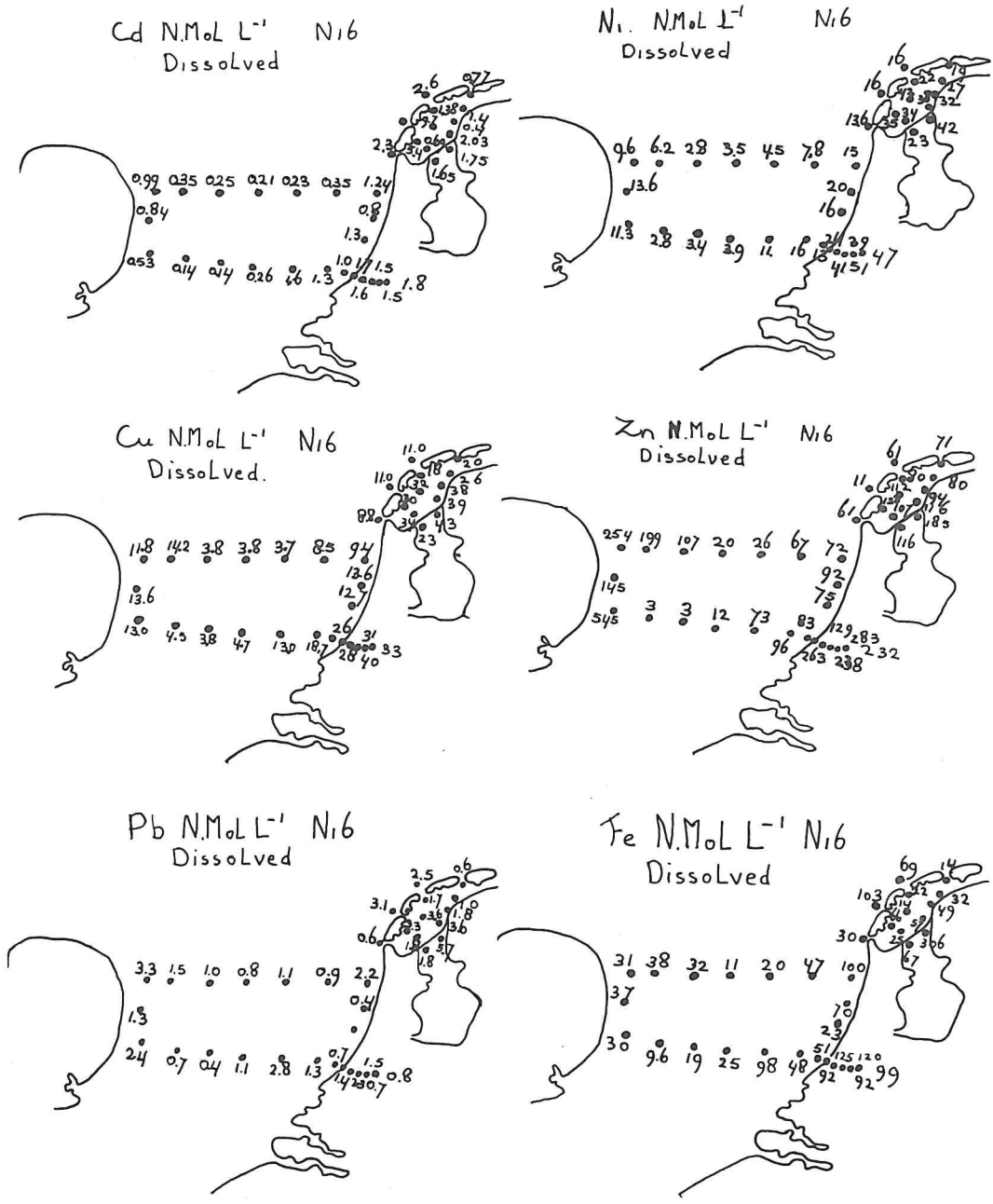


Fig. 22. Concentration of Cd, Cu, Ni, Zn, Pb and Fe (in $\text{nmol}\cdot\text{l}^{-1}$) plotted against station number during trip N16, also including some data obtained during trip W43.

8. REFERENCES

- ABDULLAH, M.I., O.A. EL-RAYIS & J.P. RILEY, 1976. Re-assessment of chelating ion-exchange resins for trace metal analysis of sea water.—*Analytica chim. Acta* 84: 363-369.
- AGEMIAN, H. & A.S.Y. CHAU, 1978. Automated method for the determination of total dissolved mercury in fresh and saline waters by ultraviolet digestion and cold vapor A.A.S.—*Analyt. Chem.* 50: 13-16.
- BAUMGARTNER, A. & E. REICHEL, 1975. *The world water balance*. Elsevier: 1-179.
- BEWERS, J.M. & P.A. YEATS, 1980. Behaviour of trace metals during estuarine mixing. Proc. SCOR/ACMR/ECOR/IAHS/UNESCO/CMG/APSO workshop on river inputs to ocean systems. Rome, 26-30 March 1979: 103-115.
- BRULAND, K.W. & R.P. FRANKS, 1983. Mn, Ni, Cu, Zn and Cd in the western North Atlantic. In: C.S. WONG, B. BOYLE, K.W. BRULAND, J.D. BURTON & E.D. GOLDBERG. Trace metals in sea water. NATO Conference Series. Plenum Publishing Corporations: 395-414.
- BRULAND, K.W., R.P. FRANKS, G.A. KNAUER & J.H. MARTIN, 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in sea water.—*Analytical chim. Acta* 105: 233-245.
- BURTON, J.D. & P.S. LISS, 1976. *Estuarine chemistry*. Academic Press, London.
- BOYLE ED. & S. HUESTED, 1983. Aspects of the surface distributions of copper, cadmium and lead in the north Atlantic and north Pacific. In: C.S. WONG, B. BOYLE, K.W. BRULAND, J.D. BURTON & J.D. GOLDBERG. Trace metals in sea water. NATO Conference Series. Plenum Publishing Corporations: 379-394.
- DUINKER, J.C., 1976. Mobilization of metals in the Dutch Wadden Sea. In: A.D. McINTYRE & F. MILLS. *Ecological toxicology research*. Plenum Publishers Corporation, New York: 167-176.
- , 1980. Suspended matter in estuaries: adsorption and desorption processes. In: E. OLAUSSON & I. CATO. *J. Wiley & Sons*: 121-151.
- DUINKER, J.C. & R.F. NOLTING, 1976. Distribution model for particulate trace metals in the Rhine estuary, Southern Bight and Dutch Wadden Sea.—*Neth J. Sea Res.* 10: 71-102.
- , 1977. Dissolved and particulate trace metals in the Rhine estuary and Southern Bight.—*Mar. Pollut. Bull.* 8 (3): 65-71.
- , 1978. Mixing, removal and mobilization of trace metals in the Rhine estuary.—*Neth. J. Sea Res.* 12: 205-223.
- , 1982. Dissolved copper, zinc and cadmium in the Southern Bight of the North Sea.—*Mar. Pollut. Bull.* 13: 93-96.
- DANIELSSON, L.G., 1980. Cadmium, cobalt, copper, iron, lead, nickel and zinc in Indian ocean water.—*Mar. Chem.* 8: 199-215.
- DANIELSSON, L.G., B. MAGNUSSON & S. WESTERLUND, 1978. An improved metal extraction procedure for the determination of trace metals in sea water by A.A.S. with electrothermal atomization.—*Analyt. chim. Acta* 98: 47-57.
- DANIELSSON, L.G. & S. WESTERLUND, 1983. Trace metals in the arctic ocean. In: C.S. WONG, B. BOYLE, K.W. BRULAND, J.D. BURTON & E.D. GOLDBERG. Trace metals in sea water. NATO Conference Series. Plenum Publishing Corporations: 85-95.
- FEELEY, R.A. & G.J. MASSOTH, 1981. Major and trace-element composition of suspended matter in the north-east Gulf of Alaska: relationships with major sources.—*Analyt. Chem.* 52 (4): 741-746.
- GOLDBERG, ED., 1972. Man's role in the major sedimentary cycle. In: D. Dyrssen & D. Jagner. *The changing chemistry of the oceans*. Wiley Interscience: 267-288.
- MEADE, R.H., 1972. Transport and deposition of sediments in estuaries.—*Mem. geol. Soc. Am.* 133: 91-120.
- MAGNUSSON, B., L.G. DANIELSSON & S. WESTERLUND, 1981. Solvent extraction procedures combined with backextraction for trace metal determinations by A.A.S.—*Analyt. chim. Acta* 131: 63-72.
- MARTIN, J.M. & M. MEYBECK, 1979. Elemental mass-balance of material carried by world major rivers.—*Mar. Chem.* 7: 173-206.
- MARTIN, J.M. AND M. WHITFIELD, 1981. The significance of the river input of chemical elements to the ocean. In: C.S. WONG, B. BOYLE, K.W. BRULAND, J.D. BURTON & E.D. GOLDBERG. Trace metals in the sea. NATO Conference Series. Plenum Publishing Corporations: 266-296.

- PRICE, N.B. & S.E. CALVERT, 1973. A study of the geochemistry of suspended particulate matter in coastal waters.—*Mar. Chem.* 1: 169-189.
- RANTALA, R.R. & D.H. LORING, 1977. A rapid determination of 10 elements in marine suspended particulate matter by atomic absorption spectrophotometry.—*At. Absorpt. Newsl.* 16: 51-52.
- SHOLKOVITZ, E.R., 1978. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater.—*Geochim. cosmochim. Acta* 40: 831-845.
- SHOLKOVITZ, E.R. & N.B. PRICE, 1980. The major element chemistry of suspended matter in the Amazon estuary.—*Geochim. cosmochim. Acta* 44: 163-171.
- SUNDBY, B., 1974. Distribution and transport of suspended particulate matter in the Gulf of St. Lawrence.—*Can J. Earth Scis* 11: 1517-1533.
- SUNDBY, B. & D.H. LORING, 1978. Geochemistry of suspended particulate matter in the Saguenay Fjord.—*Can. J. Earth Scis* 15: 1002-1011.
- SKEI, J.M. & S. MELSON, 1982. Seasonal and vertical variations in the chemical composition of suspended particulate matter in an oxygen-deficient fjord.—*Estuar. coast. Shelf Sci.* 14: 61-78.
- STRICKLAND, J.D.H. & T.R. PARSONS, 1972. A practical handbook of sea water analysis.—*Bull. Fish. Res. Bd Can.* 167: 245-249.
- TUREKIAN, K.K., 1977. The fate of metals in the oceans.—*Geochim. cosmochim. Acta* 41: 1139-1144.
- YEATS, P.A. & J.A. CAMPBELL, 1983. Ni, Cu, Cd and Zn in the northwest Atlantic Ocean.—*Mar. Chem.* 12: 43-58.
- YENTSCH, C.S. & D.W. MENZEL, 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence.—*Deep Sea Res.* 10: 221-232.

TABLE 2
Concentration of dissolved trace metals (Cu, Zn, Pb, Fe, Ni and Cd) in the western Wadden Sea.

Date Sample (1984) no.	Positions	Time	Filter no.	Salinity (‰)	Temp-ature (°C)	Depth (m)	pH	Susp. matter ++	Cd +	Zn +	Ni +	Cu +	Pb +	Fe +						
30-1	BD-1	53° 3' 12" NB 4° 58' EL	BD-1	24.2	3.9	10.00	7.89	16.7	601.80	5.35	8092	123	2067	35.20	1895	29.82	700	3.38	3700	66.25
	BD-3	53° 3' 18" NB 5° 2' 12" EL	BD-3	19.0	2.2	14.50	7.81	12.5	957.90	8.52	9044	138	2467	42.02	2257	35.52	925	4.46	5400	96.68
	BD-4	53° 2' 12" NB 5° 6' 40" EL	BD-4	17.5	2.6	9.50	7.86	16.4	1097.20	9.76	7616	116	2467	42.02	2092	32.92	1075	5.18	1200	21.48
	BD-5	53° 4' NB 5° 16' 42" EL	BD-5	14.3	3.0	12.00	7.94	19.3	214.50	1.90	7378	112	2400	40.87	2018	32.75	275	1.32	600	10.74
	BD-6	53° 14' 44" NB 5° 10' EL	BD-6	29.7	3.1	8.50	7.89	77.6	130.70	1.16	5236	80	1250	21.29	1096	17.24	200	0.96	800	14.32
	BD-7	53° 19' 36" NB 5° 9' 12" EL	BD-7	30.0	2.9	15.55	7.89	42.3	155.70	1.38	5474	83	1283	21.85	1170	18.41	175	0.84	1400	25.06
31-1	BD-8	53° 21' 18" NB 5° 13' 30" EL	BD-8	27.0	2.8	7.00	7.88	36.9	62.08	0.55	5474	83	1250	21.29	1458	22.94	362	1.74	800	14.32
	BD-9	53° 21' 12" NB 5° 19' 48" EL	BD-9	27.7	2.1	7.00	7.84	43.1	138.80	1.23	5355	82	1350	22.99	1170	18.41	325	1.56	650	11.63
	BD-10	53° 21' 54" NB 5° 23' 24" EL	BD-10	25.8	2.1	1.30	7.88	24.0	62.08	0.55	2618	40	800	13.62	717	11.28	175	0.84	349	6.26
	BD-11	53° 26' 36" NB 5° 35' 48" EL	BD-11	29.5	2.9	8.00	7.89	42.6	86.59	0.77	4641	71	1150	19.58	1293	20.35	125	0.60	769	13.77
	BD-12	53° 24' 40" NB 5° 38' 30" EL	BD-12	29.2	3.7	11.50	7.86	79.4	78.42	0.69	2975	45	1133	19.29	1129	17.76	250	1.20	734	13.14
	BD-13	53° 24' 12" NB 5° 14' 6" EL	BD-13	30.0	2.6	6.50	7.83	117.0	19.05	1.70	6783	103	1417	24.13	1211	19.05	760	7.60	15678	280.00
	BD-14	53° 23' 30" NB 5° 49' 12" EL	BD-14	30.4	2.6	5.50	7.83	352.8	196.06	1.74	5236	80	1283	21.85	955	15.03	800	2.89	9626	172.37
	BD-15	53° 23' 42" NB 5° 50' 36" EL	BD-15	30.4	2.6	5.50	7.86	173.7	179.72	1.59	4522	69	1217	20.72	930	14.63	275	1.32	5209	93.20
1-2	BD-16	53° 24' NB 5° 40' 12" EL	BD-16	29.6	2.7	6.50	7.85	54.9	142.14	1.26	4760	73	1150	19.58	1013	15.94	175	0.84	3339	59.78
	BD-17	53° 20' 12" NB 5° 38' 12" EL	BD-17	22.0	1.9	3.50	7.83	50.9	161.75	1.43	5593	85	1583	26.96	1392	21.90	400	1.93	1835	32.86
	BD-18	53° 19' 16" NB 5° 34' 18" EL	BD-18	17.2	1.6	1.50	7.87	47.1	78.42	0.69	5831	89	1583	26.90	1540	24.23	125	0.6	2202	39.42
	BD-19	53° 17' 36" NB 5° 28' EL	BD-19	16.0	1.8	8.50	7.92	140.7	122.54	1.09	6420	98	1550	26.40	1474	23.19	212	1.02	1101	19.72
	BD-20	53° 15' 12" NB 5° 26' 42" EL	BD-20	11.2	1.9	1.40	7.98	726.2	45.75	0.40	6188	94	1900	32.36	1688	26.56	150	0.72	11365	203.00
2-2	BD-21	53° 7' 18" NB 5° 22' 40" EL	BD-21	6.5	2.0	4.50	7.95	70.5	39.21	0.34	6188	94	2167	36.91	2410	37.93	375	1.80	2762	49.45
	BD-22	53° 5' 42" NB 5° 22' 6" EL	BD-22	11.6	2.0	6.00	7.95	43.4	228.74	2.03	7616	116	2217	37.76	2533	39.86	750	3.60	3181.7	56.96
	BD-23	53° 3' 12" NB 5° 21' 24" EL	BD-23	0.7	1.7	4.50	8.25	6.7	197.70	1.75	12138	185	2500	42.58	2754	43.34	1187	5.73	17114	306.00
	BD-24	53° 54' 24" NB 5° 7' 36" EL	BD-24	0.7	2.2	4.50	8.17	26.6	176.46	1.56	7616	116	1367	23.28	2639	41.53	362	1.75	3758	67.29
	BD-25	53° 57' 30" NB 5° 0' 24" EL	BD-25	16.2	2.6	-	7.89	59.1	78.42	0.69	7021	107	2050	34.91	1724	27.60	362	1.75	1400	25.06

+ 10⁻¹ -1 ++ 10⁻¹ -1 +++ 10⁻¹ -1

TABLE 3

Concentration of Si, Al, Mn, Zn, Fe, Mg, Ca and K in suspended particulate matter in the western Wadden Sea (leachable and total concentration; also percentage leachable of total concentration is given).

Sample no.	Susp. matter (mg·l ⁻¹)	Si %		Al %		Mn (µg·g ⁻¹)		Zn (µg·g ⁻¹)		Fe %		Mg %		Ca %		K %		
		total	%leach-able	total	%leach-able	total	%leach-able	total	%leach-able	total	%leach-able	total	%leach-able	total	%leach-able	total	%leach-able	
BD-1	16.7	16.08	5.28	869.22	1103	79	266.10	415	64	1.20	3.74	32	0.56	1.14	9.73	9.88	0.14	0.89
BD-3	12.5	16.11	5.40	967.74	1156	84	400.00	500	71	1.33	3.75	35	0.57	1.14	7.50	7.60	0.18	0.94
BD-4	16.4	18.42	5.73	884.14	1151	77	338.41	490	70	1.14	3.79	30	0.47	1.12	8.00	8.16	0.12	0.92
BD-5	19.3	15.65	5.17	917.09	1144	80	299.22	428	70	1.08	3.43	31	0.46	1.01	7.12	7.24	0.12	0.93
BD-6	77.6	14.38	5.08	727.10	858	85	270.19	354	76	1.14	3.63	31	0.50	1.10	7.37	7.51	0.12	0.26
BD-7	42.3	15.91	5.69	800.72	956	84	183.80	278	66	0.98	3.41	29	0.52	1.10	7.24	7.39	0.11	1.23
BD-8	36.9	13.80	4.93	829.26	956	86	225.82	328	69	1.05	3.18	33	0.52	1.03	9.31	9.42	0.11	1.02
BD-9	43.1	17.26	5.72	785.85	949	83	180.45	284	64	0.96	3.49	27	0.51	1.12	6.56	6.80	0.09	1.21
BD-10	24.0	17.95	6.12	873.64	1069	82	239.73	364	65	1.13	3.78	30	0.53	1.18	9.37	9.69	0.11	1.11
BD-11	42.6	17.62	4.31	757.23	916	83	182.57	264	69	0.97	3.07	31	0.48	1.04	8.36	8.53	0.10	1.36
BD-12	79.4	17.03	5.63	781.75	930	84	174.91	263	66	0.85	3.30	26	0.49	1.13	6.29	7.13	0.08	1.46
BD-13	117.0	20.67	4.83	578.98	712	82	132.95	200	66	0.62	2.85	22	0.36	0.86	6.33	6.51	0.07	1.55
BD-14	352.8	21.17	4.83	566.89	700	81	138.81	199	69	0.60	2.48	24	0.44	1.01	7.97	8.14	0.05	1.43
BD-15	173.7	22.95	4.99	824.55	973	85	150.32	219	68	0.66	2.67	25	0.48	1.11	7.19	7.35	0.07	1.47
BD-16	54.9	15.28	4.41	765.85	920	83	172.02	277	62	0.93	3.27	28	0.48	1.11	6.74	6.89	0.07	1.63
BD-17	50.9	16.93	4.67	827.12	981	84	197.23	295	67	0.93	3.32	28	0.49	1.03	6.94	7.05	0.08	1.52
BD-18	47.1	14.96	5.14	770.49	910	83	212.31	308	69	0.91	3.09	29	0.45	0.98	5.89	6.10	0.10	1.13
BD-19	140.7	20.14	-	911.80	1098	83	197.00	289	68	0.94	3.35	28	0.63	1.17	8.21	8.37	0.20	1.14
BD-20	726.2	22.40	2.41	685.89	806	85	184.64	231	79	0.63	1.89	33	0.53	1.09	10.84	10.98	0.07	0.63
BD-21	70.5	14.72	3.21	903.68	1036	87	267.92	356	75	0.84	2.90	29	0.55	1.02	6.85	6.96	0.17	1.11
BD-22	43.4	15.34	5.15	929.08	1091	85	268.80	372	72	1.00	3.23	31	0.64	1.18	6.82	6.91	0.07	1.15
BD-23	6.7	2.00	1.96	1203.65	1436	84	746.26	1014	74	1.65	3.45	98	0.33	0.63	4.86	4.75	98	-
BD-24	26.6	14.51	4.19	1152.07	1328	87	584.58	735	79	1.01	2.83	36	0.46	0.91	4.93	4.99	99	0.86
BD-25	59.1	15.96	5.12	900.60	1033	87	244.39	342	71	0.91	3.11	27	0.61	1.08	7.51	7.71	0.20	1.24

TABLE 4
Concentration of dissolved trace metals (Cu, Zn, Pb, Fe, Ni and Cd) in the Southern Bight.

Filter no.	Station no.	Cu		Zn		Pb		Fe		Ni		Cd	
		+	+++	++	+++	+	+++	++	+++	+	+++	+	+++
26	1	698	10.98	3.87	59.20	660	3.17	5.77	103.30	933	15.89	-	-
42	2	716	11.27	3.97	60.87	530	2.54	3.84	68.86	933	15.89	300	2.66
44	3	867	13.64	6.02	92.09	85	0.40	3.92	70.24	1200	20.44	86	0.76
45	4	811	12.76	4.89	74.92	30	0.14	1.31	23.40	966	16.45	153	1.36
46	5	2111	32.22	15.20	232.52	155	0.75	5.54	99.16	2800	47.69	205	1.82
47	6	1943	30.57	15.60	238.64	180	0.86	5.15	92.26	3000	51.09	171	1.52
48	7	2496	39.29	18.80	287.59	154	0.74	6.72	120.30	2333	39.73	176	1.56
49	8	1773	27.90	17.20	263.11	480	2.30	8.86	158.71	2400	40.88	183	1.62
50	9	1113	17.51	8.46	129.55	285	1.37	5.15	92.26	1400	23.84	196	1.75
52	10	1660	26.12	5.41	82.73	135	0.65	2.84	50.96	800	13.62	114	1.01
53	11	1188	18.69	6.32	96.77	280	1.34	2.69	48.20	933	15.89	147	1.30
54	12	811	12.76	4.79	73.36	590	2.83	5.46	97.78	666	11.34	183	1.62
55	13	301	4.73	0.81	12.39	240	1.15	1.38	24.78	233	3.96	30	0.26
55	13	867	13.64	3.36	51.39	629	2.98	11.54	199.72	266	4.53	16	0.14
56	14	245	3.85	0.20	3.05	75	0.36	10.70	190.26	200	3.40	16	0.14
56	14	415	6.53	1.00	15.29	210	1.01	11.38	203.84	1133	19.29	130	1.15
57	15	283	4.45	0.20	3.05	135	0.65	0.54	9.63	166	2.83	16	0.14
57	15	528	8.31	6.53	15.29	325	1.56	16.52	295.85	200	3.40	23	0.21
58	16	830	13.06	33.90	518.58	500	2.40	1.84	30.05	666	11.34	60	0.63
43	17	867	13.64	9.48	145.15	660	3.17	2.07	37.17	800	13.62	94	0.84
59	18	754	11.86	16.60	254.39	680	3.27	1.76	31.63	566	9.64	112	0.99
61	19	905	14.24	13.06	199.78	325	1.56	2.15	38.55	866	6.23	40	0.35
62	20	245	3.85	7.04	107.69	210	1.01	1.77	31.67	166	2.82	28	0.25
62	20	301	4.73	12.55	192.00	210	1.01	15.45	276.90	260	4.43	24	0.21
63	21	245	3.85	1.30	19.88	160	0.77	0.61	11.01	206	3.50	24	0.21
63	21	245	3.85	3.30	50.48	285	1.37	12.30	2.20	300	5.11	200	1.77
64	22	236	3.71	1.70	26.00	230	1.10	1.15	20.64	266	4.53	26	0.23
64	22	358	5.63	1.20	18.35	285	1.37	-	-	500	8.51	376	3.34
65	23	545	8.57	4.38	67.11	180	0.86	2.61	46.82	460	7.83	40	0.35
65	23	418	6.57	32.10	491.05	410	1.97	16.60	298.42	733	12.48	200	1.78
66	24	600	9.44	4.69	71.80	460	2.21	5.61	100.54	900	15.32	140	1.24
67	25	563	8.86	3.97	60.73	125	0.60	1.69	30.29	800	13.62	260	2.31

+ ng.l⁻¹++ µg.l⁻¹+++ nmol.l⁻¹

TABLE 5
Concentration of Si, Al, Ca, Mg, Fe, Mn, Zn, Cu, Cd and Ni in suspended particulate matter in the Southern Bight (total concentration).

Date 1984	Time	Positions	Stat. no.	Depth (°/oo)	Salin- ity (°/oo)	Tempe- rature (°C)	pH	Susp. matter +	Si %	Al %	Ca %	Mg %	Fe %	Mn	Zn	Cu	Cd	Ni
27-2	12.30	53°15'00''NB 4°48'02''EL	1	17.5	32.40	4.0	8.12	24.2	14.56	2.80	3.85	0.93	2.06	630	155	74	2.99	21.69
15.15		53°25'05''NB 5°03'00''EL	2	25	32.30	3.1	8.22	12.6	17.98	3.96	5.08	1.23	2.23	770	230	119	2.84	19.84
28-2	8.25	52°26'00''NB 4°31'00''EL	3	13	27.30	3.7	7.89	19.2	16.62	3.90	2.59	0.87	3.09	1067	390	115	2.60	26.04
10.00		52°14'00''NB 4°21'00''EL	4	15	31.80	3.9	7.96	17.8	16.97	4.08	3.59	1.09	2.63	955	286	106	2.38	14.04
13.30		Rhine	5		1.00	4.5	7.77	9.4	19.64	5.07	3.13	1.03	2.63	1170	342	414	16.75	55.85
14.30		Rhine	6		6.40	4.6	7.62	17.5	15.34	4.41	5.17	1.36	3.21	885	571	291	8.14	68.80
14.50		Rhine	7		11.40	4.8	7.65	11.7	16.75	4.32	2.97	1.76	3.14	870	342	196	5.76	76.92
14.55		Rhine	8		15.20	4.8	7.68	19.3	17.39	4.11	2.35	0.86	3.56	1005	474	212	4.79	39.64
15.20		Rhine	9		23.00	5.1	7.83	19.5	16.35	4.31	3.55	1.02	3.20	882	359	174	4.87	38.54
15.35		52°00'05''EL 4°03'05''EL	10	15	30.50	4.8	7.95	20.3	16.12	4.92	6.69	0.89	3.38	1034	369	147		32.00
17.00		52°05'05''NB 3°49'00''EL	11	26	28.40	4.5	7.96	15.0	16.78	3.48	3.20	0.77	3.33	900	360	146	5.66	25.00
18.15		52°07'05''NB 3°33'00''EL	12	28	31.50	4.5	8.02	7.2	17.48	4.41	4.07	1.16	3.47	972	403	160	4.16	20.80
19.45		52°05'00''NB 3°15'00''EL	13	30	35.10	5.4	8.05	3.7	18.43	3.43	6.04	1.74	2.52	1081	338	189		10.10
21.00		52°09'00''NB 2°53'00''EL	14	40	35.35	5.9	8.07	6.4	10.65	2.83	5.41	1.22	2.55	443	258	359	7.42	15.62
23.00		52°09'00''NB 2°30'00''EL	15	40	35.40	6.5	8.06	13.7	5.53	4.31	5.25	1.12	2.73	401	212	88	1.64	27.37
29-2	10.00	52°11'00''NB 2°05'00''EL	16	42	35.16	5.6	8.03	24.6	16.70	5.19	2.72	0.93	3.44	448	153	81	2.54	26.42
12.00		52°25'00''NB 2°55'00''EL	17	45	34.35	4.1	8.00	35.0	17.02	5.32	2.59	1.10	3.39	634	154	75	1.35	30.71
14.00		52°40'00''NB 2°15'00''EL	18	45	34.55	4.3	8.00	16.6	18.40	4.65	2.57	0.94	3.20	572	198	102		58.73
15.30		52°39'00''NB 2°21'00''EL	19	42	35.32	6.0	8.03	16.2	20.30	5.61	3.78	1.15	3.29	524	154	80	2.46	32.41
17.40		52°40'00''NB 3°03'00''EL	20	34	35.50	6.2	8.06	9.1	15.49	3.99	4.68	1.27	2.40	439	230	153	2.66	24.72
19.35		52°40'00''NB 3°27'00''EL	21	28	35.43	5.6	8.04	6.2	18.95	3.29	6.01	1.25	2.01	403	266	145	2.82	48.38
21.30		52°40'00''NB 3°50'00''EL	22	28	35.00	4.9	8.00	5.4	17.40	3.36	5.13	1.32	2.31	462	379	240	8.33	16.51
1-3	8.00	52°40'00''NB 4°15'00''EL	23	25	33.13	4.4	8.02	11.7	18.07	3.49	5.01	1.16	2.40	603	282	102	7.26	19.23
10.00		52°40'00''NB 4°30'00''EL	24	17	32.30	4.4	7.90	15.0	18.80	3.48	4.42	0.86	2.70	866	233	140	2.83	25.00
11.45		52°51'00''NB 4°37'00''EL	25	14	32.70	4.4	8.01	31.3	18.01	3.62	6.47	0.86	2.79	895	319	74	1.99	19.96

+ mg.l⁻¹ ++ µg.g⁻¹

